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Physics, Chemistry, and Materials Science of Clusters

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1. Thermal and Transport Properties of Granular Metal Films: Experimental Results[†]

K.M. Unruh and J.R. Beamish
Department of Physics and Astronomy
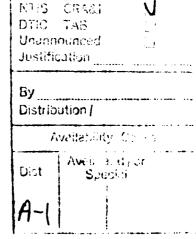University of Delaware
Newark, Delaware 19716

A systematic experimental study of various thermal and transport properties of granular materials has been carried out. Most of these materials have been prepared by sputter deposition although, in several cases, mechanical techniques have also been used. In particular, the melting behavior of $(Sn, Bi, Pb)_x(SiO_2)_{100-x}$ and Pb_xCu_{100-x} granular materials has been studied by differential scanning calorimetry, x-ray diffraction, and transmission electron microscopy. At high metal concentrations these granular films are characterized by large connected metal particles widely distributed in size. As the metal concentration is reduced the mean particle size is also reduced and the particle size distribution becomes more uniform. Corresponding to the decrease in the metal particle size a corresponding decrease in the metal temperature has been observed. By considering the effects of a constraining matrix, melting point enhancements are also expected for intermediate sized particles; this effect has not currently been observed.

Transport measurements in granular $(Ni, Cu, W)_x(SiO_2)_{100-x}$ thin films have also been carried out from room temperature to below 100 mK and, at selected temperatures, in applied magnetic fields as large as 6 T. As the metal concentration is reduced, the temperature coefficient of the resistance (TCR) at room temperature changes from positive to negative as the conduction mechanism changes from metallic transport along connected metal particles to tunneling between isolated particles. The details of the temperature and composition dependence of the resistance, however, are system dependent. In the $Ni-SiO_2$ granular system, for example, the room temperature TCR changes sign at a nominal Ni concentration of about 70 atomic percent (38 volume percent). Samples with Ni concentrations greater than 70 percent exhibit a minimum in the temperature dependence of the resistance that moves to progressively lower temperatures with increasing Ni concentration. The temperature dependence of the resistance of samples with Ni concentrations less than 70 percent can be well described, from room temperature to about 5 K, by an expression of the form $\rho(T) \sim \exp[T_0/T)^\alpha]$ where T_0 monotonically increases with decreasing Ni concentration and $\alpha \approx \frac{1}{2}$. Below about 5 K, however, a crossover to a weaker temperature dependence of the resistance characterized by a common value of T_0 has been observed. All the studied $Ni-SiO_2$ samples exhibit a negative magnetoresistance, unlike in the $Cu-SiO_2$ system where the magnetoresistance changes sign as a function of the temperature.

2. Thermal and Transport Properties of Granular Metals: Theory

Ping Sheng
Exxon Research and Engineering Company
Clinton Township, Route 22 East
Annandale, New Jersey 08801

The melting characteristics of small metal particles embedded in an elastic matrix is examined through the mean-field theory and the consideration of the elastic matrix environment. It is found that while the small size of the particles tends to lower the melting temperature, the elastic confinement effect of the matrix can enhance the melting point. It is also found that the anharmonic effect becomes more pronounced as the particle size decreases to below 60 Å, causing a significant drop of the Debeye temperature that has been observed experimentally in Fe particles.

The electronic transport characteristics in granular metals can be divided into two regimes. In the metal-rich regime the electrons are transported through the connected metallic channels. It can be shown that in the regime the low temperature conductivity exhibits two dimensional localization effects observable through the logarithmic temperature dependence of the conductivity. In addition, under a magnetic field the quantum interference effect due to electron's wave-like nature can lead to oscillating magnetoresistance. For the insulator-rich regime, on the other hand, electronic transport is mainly due to hopping conductivity between the metal grains, and the granular system provides a realization of the theoretical model where electron-electron interaction plays a dominant role in system's transport behavior. Theoretical consideration can lead to the prediction of the observed $\exp(-T^{-1/2})$ dependence of the conductivity on temperature, with a crossover into $\exp(-T^{-1/4})$ dependence at low temperatures. Systematic experimental study may lead to a verification of these behaviors as well as clarify the nature of electronic density of states in the granular systems.

3. Nanostructure-Induced Properties of Granular Metallic Solids[†]

C.L. Chien
Department of Physics and Astronomy
The Johns Hopkins University
Baltimore, Maryland 21218

Granular metallic solids consist of ultrafine metal granules imbedded in an insulating or, less frequently, in a metallic medium. They can be most conveniently fabricated by physical vapor deposition (e.g. high-rate sputtering). The ultrafine granules, as small as 15Å, can be elemental metals, crystalline alloys or amorphous alloys. The physical properties of these nanocomposites are dictated by the granules and, more importantly, by the nanostructures. Consequently, their properties can be tailored by controlling the granule size, metal volume fraction and connectivity of the granules. Enhances physical properties (magnetic, mechanical, lattice dynamics, corrosion, optical, superconducting, etc.), as a result of the intricate nanostructure, will be described.

4. The Assembly of Supra Nanoclusters Within Crystalline 3-D Surfaces[†]

Jim MacDougall and Galen Stucky
Department of Chemistry
University of California
Santa Barbara, California 93106

Thomas Bein and Karin Moller
Department of Chemistry
University of New Mexico
Albuquerque, New Mexico 87131

Norman Herron and Ying Wang
E.I. du Pont de Nemours
Wilmington, Delaware

By using nanoporous crystalline inorganic hosts with 0 (clathrated), 1 (1-d tunnel systems), 2 (layered and 2-d cage/tunnel), and 3 (3-d cage/tunnel) connectivity patterns, ordered arrays of small semiconductor and molecular clusters can be constructed by the self assembly of inorganic and organic precursors. The ability to alter the host surface topography allows one to selectively control cluster geometry and to define intercluster properties. The presentation will discuss the synthesis and characterization of I-VII, II-VI, III-V and II-V clusters (< 15 Å in diameter) in various host configurations and glasses.

5. Dynamical Processes of Gas Phase Clusters

R.R. Lucchese and W.H. Marlow
Texas A&M University
College Station, Texas 77843

The objective of this project is to establish the basis for kinetic modelling of cluster formation and growth in the gas phase. Our research is the development of theoretical and computational methods treating thermal collisions of clusters in the presence of a background gas. It includes the factors of composition and structure that determine formation cross sections for cluster-cluster coagulational collisions and provides the means by which the resulting distributions of cluster structures and of internal energies can be estimated. As a complementary undertaking, phenomenological descriptions of both coagulation rates and energy accommodation are being developed and compared in detail with the corresponding simulation descriptions.

6. Semiconductor Interface Formation by Atom and Cluster Deposition

J.H. Weaver
Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

Abrupt interfaces with no observed substrate disruption are produced by a novel method of metal-semiconductor junction formation. This method involves the condensation of a thin Xe buffer layer on cleaved surfaces to isolate the semiconductor from impinging metal atoms. The Xe buffer layer provides a surface upon which the metal atoms diffuse, nucleate, and grow into metallic clusters. These clusters are then brought into contact with the substrate when the Xe is thermally desorbed. The result is an abrupt, non-disrupted, nearly-ideal interface. Photoemission studies of Al, Ag, Au, Ga, Ti, and Co clusters grown on n- and p-GaAs(110) show unique Fermi level positions ~0.3 and 1.0 eV below the conduction band minimum, respectively, that are nearly metal- and coverage-independent. We find no evidence that metal-induced gap states or conventional defect levels are important in determining the Fermi level position in the gap, but photoemission results indicate surface unrelaxation around the clusters. This unrelaxation results in the reappearance of state in the gap. High-resolution electron microscopy results for Au(clusters)/GaAs(110) show intimate contact with no intermixing at the interface, with sintering of Au clusters to form an interconnected network of metal islands at high coverages. Comparisons of these results with those for interfaces formed by atom deposition at 60 and 300 K emphasize the novel properties of the cluster interface.

7. Chemical Reactivity and Electronic Properties of Silicon Microclusters

Daniel A. Jelski
Department of Chemistry
State University of New York, College at Fredonia
Fredonia, New York 14063

Tapio T. Rantala[†] and Thomas F. George
Departments of Chemistry and Physics & Astronomy
State University of New York at Buffalo
Buffalo, New York 14260

The tight-binding model is used to study the reactivity and electronic properties of silicon clusters, ranging in size from 10 to 60 atoms. This model is shown to yield accurate data with respect to the one-electron levels near the Fermi level. Using this method, it is possible to generate different structures, charge distributions, bond strengths and optical properties. Three topics are addressed below.

The first topic is the class of silicon clusters containing 30 to 45 atoms. These clusters are found to react with nucleophiles such as ammonia and methanol at rates which are a strong function of cluster size. A periodicity of approximately 6 atoms is observed, with Si_{36}^+ and Si_{42}^+ being most reactive, and Si_{39}^+ being much less so. The reaction rates vary over two orders of magnitude. A model is presented to account for this phenomena, in which the cluster is arranged in six-membered rings, with a cap to account for the additional atoms.

The second topic concerns the structure of Si_{60}^+. The experimental photofragmentation data strongly indicates that Si_{10}^+ is the most probable daughter ion. It is suggested that Si_{60}^+ consists of stacked, naphthalene-like rings, which can then fragment along the ring plane, consistent with experiments.

The final topic is a review of the structure of Si_{10}^+. This is undertaken largely to establish the tight-binding model as an accurate method of calculation, especially for excited states. It is shown that this model yields results which are largely consistent with those of other works, but there are important differences (which will be discussed). Further, the experimentally measured photoelectron spectrum can be fully accounted for using this method, leading to the conclusion that the method yields satisfactory information for excited states near the Fermi level. The transition dipoles are thus calculated, and various optical parameters are given.

[†]Permanent address: Department of Physics, University of Oulu, 90100 Oulu 10, Finland

8. Metal-Metal and Metal-Ligand Cluster Interactions

Hua Wang, Gregory W. Smith, Yi Qin, and Emily A. Carter
Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024-1569

In the past year, we have begun ab initio electronic structural studies into the properties and chemisorptive reactivity of transition metal clusters by concentrating on issues related either to purely metallic bonding or to metal-ligand interactions. The three problems we are currently examining include: (i) the electronic structure and metal-metal bonding in low-lying states of Pd and Pt trimers (extracting cohesive energies, vibrational frequencies, and equilibrium geometries for various low-lying electronic states);[1] (ii) the differences between bonding NO versus CO to Pd and Pt atoms (NO prefers a bent geometry while CO bonds linearly to the metal atom;[2] and (iii) quantifying the influence of ancillary ligands on the preferred spin state of metal atoms in organometallic complexes and clusters, as evidenced by spin-induced changes in bond energies in the series $Mn(CO)_x^+$ (x = 1 - 6).[3] Underlying concepts and selected illustrative results from these three areas will be presented.

1. H. Wang and E.A. Carter, work in progress.
2. G.W. Smith and E.A. Carter, *J. Chem. Phys.*, to be submitted.
3. Y.Qin and E.A. Carter, work in progress.

9. Semiconductor Cluster Surface Chemistry

R.E. Smalley
Rice Quantum Institute
and Departments of Chemistry and Physics
Rice University
Houston, Texas 77251

One of the principal motivating ideas in the study of clusters is that these species might serve as "molecular models" of real surfaces. Because of the relatively small number of atoms involved and the ability to systematically vary the size, composition, net charge, etc., such clusters could serve as a crucial testing ground for the development of a firm, fundamental understanding of surfaces. With the strong predictive powers which come from fundamental understanding, our ability to engineer new surfaces, interfaces, and materials should be greatly enhanced. Semiconductors such as silicon, germanium, and gallium arsenide/phosphide have been a major focus of our early work with clusters. As with carbon, there is now good evidence that special cluster structures are adopted with all these materials. Silicon, for example, reveals specially stable and well-connected structures for clusters of 21, 33, 39, and 45 atoms which are particularly evident in their behavior toward surface chemisorption of ammonia. A variety of theoretical groups have now considered these results in detail. The emerging picture is that these clusters have four-connected "inside" atoms much like the diamond lattice of bulk silicon, while the outer surface is knitted together with much the same bonding patterns as those found on the various reconstructed surfaces of low miller index planes of silicon single crystals.

10. Size Dependence of the Reactivity and the Dynamics of Small Gaseous Clusters

Li Song, Alex Eychmuller, H.J. Hwang, Dilip Sensharma and M.A. El-Sayed
Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024-1569

Two different types of size dependence studies are made; one involves the chemical reactivity of metal cluster (Nb_x) and the other examines the mechanisms of evaporation of $(CsI)_n$ molecules ($n = 1, 2$ and 3) from gaseous ionic alkali halide $[Cs(CsI)_x]^+$ clusters, with $x = 2-15$.

In the first study, we have examined the reaction between gaseous niobium clusters (Nb_x) and different molecules tailored to answer different questions regarding the size dependence of chemical reactivity, e.g. stereochemical specificity, competitive vs. parallel reactions.

In the second study, the rates and kinetic energy release of the evaporation of $(CsI)_n$, with $n = 1-3$, from $[Cs(CsI)_x]^+$ clusters are determined. The variation of these parameters with the size of the different boiling (dissociating) clusters strongly suggests a statistical evaporation with near zero reverse activation energies. For $n > 1$, fission seems to be favored over sequential single evaporation.

11. FTMS Studies of Cluster Ions Formed by Direct Laser Vaporization

Stephen W. McElvany
Code 6111 / Chemistry Division
Naval Research Laboratory
Washington, D.C. 20375-5000

Cluster research at the Naval Research Laboratory has utilized a variety of mass spectrometric techniques to probe the stabilities, reactions and structures of cluster ions. These cluster ions have been produced by either fast atom bombardment (sputtering) or direct laser vaporization (DLV) of solid samples. Several studies have been performed comparing these cluster production methods and possible implications on cluster formation mechanisms. A review of the results obtained using Fourier transform ion cyclotron resonance mass spectrometry (FTMS) for the analysis of laser vaporized cluster ions will be presented. The ion trapping capability of the FTMS allows the study of cluster ion/molecule reactions in addition to collision-induced dissociation (CID) and photodissociation. Cluster systems studied to date include carbon, silicon and several main group metals (Al, Ga, In, Sb and Bi). This talk will emphasize results obtained on carbon cluster ions, C_n^+ ($1 < n < 200$). In addition to studies on the formation mechanisms of carbon clusters, extensive ion/molecule reactions have been investigated to probe their reactivity and structure. Abrupt changes in reactivity can be attributed to a change in cluster structure, e.g. a linear to cyclic structural transition occurs between $n = 9$ and 10 for C_n^+. The most satisfying result of the reactivity studies has been the detection of structural isomers (linear and cyclic) for $n = 7, 8$ and 9 cluster ions. Recent interests have focused on the formation and properties of heterogeneous cluster ions. These systems include mixed-metal clusters and metal carbide clusters. The metal carbide cluster ions, $M_xC_y^+$ ($x = 1\text{-}14$; $y = 1\text{-}26$), are produced by DLV of metal and carbon-containing samples and have been shown to result from reactions in the laser-generated plasma. Detailed studies of the mono-metal clusters, MC_y^+, indicate that these species exhibit distinctly different properties from the corresponding homogeneous carbon clusters.

12. Supramolecular Particles:
The Transition from the Molecular to the Solid State

Georgia C. Papaefthymiou
Francis Bitter National Magnet Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Theoretical studies of the electronic properties of metallic clusters indicate that the appearance of solid state behavior, such as the emergence of a conduction band or collective magnetic phenomena, should occur at the vicinity of N=10, where N is the number of atoms in the cluster. Experimental studies are limited due to the difficulty of obtaining isolated microclusters of such extremely small size.

In the present study the magnetic properties of a series of isolated, well-characterized molecular clusters containing an increasing number of superexchange-coupled iron ions obtained by controlled chemical synthesis are investigated, in order to study the transition region between molecular and bulk magnetic behavior. Magnetization and magnetic Mössbauer measurements on a number of representative clusters will be presented, with an emphasis on those experimental observations that establish the existence of incipient solid-state magnetic correlation effects in these molecules.

13. Measurements of the Magnetic Structure of Clusters

Louis A. Bloomfield
Department of Physics
Jesse W. Beams Laboratory of Physics
University of Virginia
Charlottesville, Virginia 22901

We are presently developing equipment and techniques to make detailed measurements of the magnetic structure of clusters. We are particularly interested in the surface versus bulk contributions to the overall magnetic moment of a cluster and expect to determine those contributions by following the development of the magnetic moment with increasing cluster size. We also expect to achieve some understanding of the couplings between internal moments that give rise to the total moment, using molecular beam electron spin resonance techniques.

Our initial focus will be the ferromagnetic transition metals and the rare earth metals. Their magnetic properties originate in localized electron spins, producing magnetic characteristics that are largely unaffected by the thermal and rotational states of the clusters.

In this talk, I will present a report of the preliminary technical and scientific experiments being undertaken at present. These experiments center on cluster beam generation and characterization, cluster mass and position determination, and characterization of our magnets.

14. The Metal ↔ Insulator Transition in Metal Clusters and Mixed Metal/Metal-Halide Clusters

Robert L. Whetten
Department of Chemistry and Biochemistry
University of California
Los Angeles, CA 90024

Electronic properties of the non-alkali metal-atomic clusters are expected to undergo a transition from insulator to metallic electronic structure at some size between the diatomic and the small-particle regime (> 10^3 atoms). Photoionization spectroscopic experiments on cluster beams of the group-III (Al_n and In_n) and group-II metals (Ba_n and Sr_n) to $n = 100$ atoms reveal drastic nonmetallic behavior at small sizes, but Al_n and In_n are observed to gradually return to the classical metallic form across the $n = 13 - 40$ range. Specific deviations from spherical shell model predictions for both metals indicate the importance of lattice crystal field, and are consistent with icosahedral structural shells. In the group-II metals, a dominance of dispersion interactions over metallic bonding is evidenced to at least $n = 55$. A general picture of these phenomena in terms of s- and p-band hybridization can account for these observations as well as for the previously documented Hg_n case.

A second type of transition occurs as a function of composition of a mixed metal/metal-halide system, $M_x(MX)_{1-x}$. As x→0, the electronic state is characterized by localized electrons, as shown by optical spectroscopic, electron binding energy, and stability experiments.[3,4] [In particular, a range of experiments on Na/NaF, Li/LiF and Na/NaCl can be accounted for with a simple F-center model, while extensive finite-temperature quantum calculations yield excellent agreement with experiment.] First evidence for the transition to the delocalized electronic states (shell structure) already known for x > 0.8 is provided by abundance measurements on the Na/NaCl system over a wide range of compositions.

1. K. E. Schriver, J. L. Persson, E. C. Honea and R. L. Whetten, submitted 10-89, revised manuscript submitted.
2. C. Bréchignac et al., Phys. Rev. Lett. 1988; M. Broyer et al. *Phys. Rev. Lett.* 1988.
3. E. C. Honea, M. L. Homer, P. Labastie and R. L. Whetten, *Phys. Rev. Lett.* 63, 394 (1989).
4. G. Rajagopal, E.C. Honea, et al., to be submitted.
5. E. C. Honea, M. L. Homer, P. Labastie and R. L. Whetten, to be submitted.

15. Metal Clusters: Structure, Dynamics, and Fusion

J. Bernholc, D. Oh, and J.-Y. Yi
Department of Physics, North Carolina State University
Raleigh, North Carolina 27695-8202

R.S. Berry, H.-P. Cheng, and J. Rose
Department of Chemistry
University of Chicago
Chicago, Illinois 60637

P. Salamon, C. Schön, R. Mrugala, S. Sieniutycz, R. Frost, and P. Basa
Department of Mathematical Sciences
San Diego State University
San Diego, California 92182

The formation of cluster materials involves assembly and fusion of clusters under the influence of chemical and surface tension forces. The metallurgical analog of this process is annealing of powders or sintering, during which the powder particles fuse and the sinter densifies. The goal of the present work is the development of a comprehensive microscopic theory of cluster fusion and the formation of cluster materials and sinters. In order to develop this theory, it is necessary to understand the systematics of cluster structures in the medium to large cluster limit, as well the dynamical properties of both isolated and fusing clusters.

The problem has been approached in a stepping stone fashion by splitting it into three mutually interdependent sub-problems: (i) via quantum-mechanical calculations of cluster energetics as well as short quantum molecular dynamics (Car-Parrinello) runs; (ii) long "classical" molecular dynamics simulations of cluster melting and fusion via the embedded atom method; and (iii) continuum theory modeling of the fusion of spheroidal particles under the influence of surface tension forces, using parameters derived in (i) and (ii).

The microscopic calculations have so far focused on prototypic clusters of Al and Cu. For Al, the Car-Parrinello method has been used to study several close-packed clusters containing up to 55 atoms. The calculations uncovered that the transformation between icosahedral and fcc bulk-type structures can occur very early in metallic clusters, i.e. around 19 atoms. For 55 atoms, the Al clusters definitely prefer fcc arrangement. The construction of an approximate embedded atom potential for Al clusters will also be discussed.

For copper clusters, density functional calculations were used to improve the existing bulk Cu embedded atom potential. The improved potential has been used for molecular dynamics simulations to determine the regions of the potential energy surfaces which need further density functional calculations. Surface melting in copper and argon clusters was studied, enabling the determination of the surface diffusion coefficient, one of the two key parameters sought for the microscopic theory of sintering. We have also carried out simulations of fusion of two large Lennard-Jones-type clusters and studied stable structures and transition states of several Cu and alkali halide clusters.

The continuum theory part of the effort has focused on the prediction of the evolving shapes of randomly-packed spheroidal particles during fusion. We have developed optimized algorithms for finding shapes of wetted solids, simulated random packing of spheroidal particles for several distributions of radii, and used network thermodynamics to describe interactions between interparticle voids. For the fusion of the two large clusters, our prediction of the motion of the grain boundary between the clusters has been corroborated by atomic resolution TEM.

16. Ionization Potentials and Electron Affinities of Semiconductor Clusters Determined via Charge Transfer Reactions

J.A. Zimmerman, S.B.H. Bach, and J.R. Eyler
Department of Chemistry
University of Florida
Gainesville, Florida 32611-2046

Charge transfer reactions of semiconductor cluster ions generated by direct laser vaporization in a Fourier transform ion cyclotron resonance (fticr) mass spectrometer have been studied in detail. By observing the occurrence or non-occurrence of such reactions between cluster ions and neutral molecules of known ionization potential (I.P.) or electron affinity (E.A.), the ionization potentials of carbon (C_n, n = 6-24), phosphorus (P_n, n = 2-4), and arsenic (As_n, n = 2-5) clusters and the electron affinity of silicon clusters (Si_n, n = 2-6) have been determined. Given the extensive "ladder" of neutral molecules for the charge transfer reactions (i.e. many compounds with closely-spaced I.P.'s or E.A.'s) we have developed, these important physical properties can be determined with an uncertainty of only a few tenths of an electron volt, which in most cases is much better than any previous determinations.

17. Threshold Photodetachment Spectroscopy of Negative Ions

T. Kitsopoulos, I.M. Waller, J.G. Loeser, C. Chick, and D.M. Neumark
Department of Chemistry
University of California
Berkeley, California 94720

We have developed a threshold photodetachment spectrometer which yields the spectrum of transitions between a mass-selected negative ion and the neutral resulting from photodetachment. The information from this instrument is in principle similar to that obtained via photoelectron spectroscopy, but the resolution is considerably higher (0.35 meV or 3 cm^{-1}). Recent results for simple systems and applications to studies of mass-selected clusters will be described.

18. Chemistry within Molecular Clusters

James F. Garvey
State University of New York, Buffalo
Buffalo, New York 14214

We will present in this talk the observation of "intramolecular" ion-molecule reactions within doubly ($n > 51$) and triply ($n > 121$) charged clusters produced via electron impact ionization of neat beams of ammonia molecules. The fragmentation pattern strongly suggests that these cluster ions consist of two (or three) singly charged ammonia cations which react separately within the bulk neutral cluster. We will also discuss other neat cluster systems $((C_2H_4F_2)_n^+$ and $\{(CH_3)_2O\}_n^+)$ in which *novel* ion-molecule chemistry is observed, primarily due to the stabilization of an unstable reactive intermediate, within the bulk cluster. Lastly, we will present our latest attempts to utilize a Smalley-type metal cluster source, to generate high quality thin films. In addition, we will show how such a source can be used to generate high temperature material and deposit it at a relatively cool substrate. By tailoring the expansion conditions, a variety of thin films may be produced with obvious industrial applications (superconducting thin films, diamond-like carbon films, patterned or multi-layered thin films, etc.).

19. Threshold Effects in Cluster Anion Photodetachment

Mark A. Johnson
Department of Chemistry
Yale University
New Haven, Connecticut 06511

Excitation of many cluster anions (e.g. C_n^-, $(CO_2)_n^-$, Ag_n^-, $(H_2O)_n^-$) near their adiabatic electron affinities results in a competition between photodetachment of the electron and photodissociation into ionic fragments. This competition is found to depend both on the excess energy above the detachment threshold and the cluster size. We have carried out detailed studies (photoelectron, photofragmentation, and absorption spectroscopies) of a few "one electron" anionic cluster systems [$(O_2)_n^-$ and $(H_2O)_n^-$)] in order to identify the important physics controlling this competition. In particular, we explore a connection between near threshold photoexcitation of anions and inelastic electron scattering with the corresponding neutral cluster.

20. Excitations of Quantum Clusters

M.V. Rama Krishna and K.B. Whaley
Department of Chemistry
University of California
Berkeley, California 94720

The dynamical properties of helium clusters are of considerable experimental and theoretical interest because of the possibility of superfluid behavior and the consequences this may have for low temperature reactions and scattering of molecular species in such clusters. We shall present microscopic calculations of collective excitations of ^{4}He clusters, based on a quantum liquid drop model including exchange symmetry effects. Various levels of theoretical treatment for excited states are discussed, all dependent upon highly accurate knowledge of the ground state wave function which is variationally determined. The evolution of the $L=0$ compressional excitations to bulk spectra indicate that the onset of roton excitations occurs at n~240 helium atoms. Extensions to the study of embedded atoms and molecules, and to other quantum clusters, will be presented. Finally, implications for experimental probes, including manifestations of superfluidity, will be discussed.

21. Many-Body Studies of Molecular Clusters[†]

Rodney J. Bartlett, D.E. Bernholdt, G. Adams[*], J.F. Stanton and M. Rittby
Quantum Theory Project
Departments of Chemistry and Physics
University of Florida
Gainesville, Florida 32611-2085

Using new methods developed for analytical gradients, vibrational frequencies, and excited states, we provide a survey of recent results on a variety of molecular clusters. Systems of interest include anions and cations of carbon clusters, silicon carbon clusters, the triborane B_3H_9 cluster, and other clusters and molecules involving borane.

[*]Permanent address: U.S. Army Ballistic Research Lab, Aberdeen Proving Ground, Maryland 21005.

22. Infrared Laser Spectroscopy of Supersonic Carbon Clusters

Richard J. Saykally
Department of Chemistry
University of California
Berkeley, California 94720

We have developed a new experiment for measuring infrared rovibrational spectra of clusters in direct absorption. The clusters are produced by UV laser vaporization and cooled to T < 10K in a supersonic expansion. Radiation from a diode laser is multipassed through the expansion and detected with gated lock-in techniques.

The initial application of this technique has been to the study of carbon clusters.[1] Antisymmetric stretching vibrations of C_3 and C_5 were measured. The rotational temperatures were near 10K, with vibrational temperatures apparently somewhat higher.

The extension of this technique to metal clusters is currently being pursued, as is a similar approach involving tunable far-IR[2] lasers.

1. J.R. Heath, A.L. Cooksy, M.H.W. Gruebele, C.A. Schmuttenmaer, and R.J. Saykally, *Science* **244**, 564 (1989).
2. R.C. Cohen, K.L. Busarow, C.A. Schmuttenaer, Y.T. Lee, and R.J. Saykally, *Chem. Phys. Lett.*, to be published.

23. Theoretical Studies of Hydrocarbon Clusters[†]

Mark R. Pederson, Koblar A. Jackson*, Warren E. Pickett and Barry M. Klein
Complex Systems Theory Branch
Naval Research Laboratory
Washington, D.C. 20375-5000

We have employed our all-electron Gaussian-orbital-based algorithm to perform geometrical optimizations on a large variety of hydrocarbon clusters ranging in sizes of ten to sixty atoms. We show that the local-density approximation predicts all bond-lengths to an accuracy of approximately one percent for benzene, methane, acetylene, ethane, ethylene and diamond. In order to learn about diamond vapor deposition, we have introduced a model of the hydrogenated carbon (111) surface which consists of ten carbon atoms tied off with twenty-one hydrogen atoms. We show that the methyl radical may be especially important in diamond growth since the resulting C-C equilibrium separation is nearly identical to that found in cubic diamond. In contrast, the acetylenic radical leads to an adsorbate C-C bond which is substantially decreased. Cohesive energies and calculations on other possible adsorbates will be presented also.

To investigate the properties of nitrogen and phosphorous impurities in diamond we have employed hydrogen terminated carbon clusters [C_5H_{12} and $C_{17}H_{36}$]. We identify deep donor levels associated with each of these prototypical n-type impurities.

In addition, recent work on a variety of ideal and defective insulating and metallic clusters will be briefly presented.

24. Fractal and Multifractal Description of Clustering Phenomena

H.E. Stanley
Center for Polymer Sciences
Department of Physics
Boston University
Boston, Massachusetts 02215

We introduce the concept of scale symmetry or "self-similarity" and discuss conditions under which cluster size distributions reflect this scale symmetry. Then we connect the behavior of the cluster size distribution to the scaling properties of the largest clusters in the system; both are described by the same parameter, a fractal dimension d_f. We illustrate this concept by discussing clusters in the hydrogen bonded network of liquid water.

Next we discuss conditions in which the distribution is characterized not by one but rather by in infinite hierarchy of fractal dimensions. Such multifractals, as they have come to be called, abound in Nature, and selected examples will be discussed. These include the behavior of clusters arising when a low-viscosity fluid is forced under pressure into a high viscosity fluid.

25. Fractal Structure and Kinetics of Cluster Growth

Feyerdoon Family
Department of Physics
Emory University
Atlanta, Georgia 30322

The formation of large clusters by binding together single particles (or monomers) occurs commonly in many important processes in physics, chemistry, biology, medicine and engineering. Our main interest will be in the study of cluster growth in colloidal and aerosol aggregation phenomena, cluster growth in gelation and thin-films, droplet growth in vapor-deposited thin films and first-order phase transitions in condensation processes, and pattern formation by the motion of interfaces in random media. We will describe methods for describing the morphology of the clusters using the concepts of fractal geometry and multifractal scaling. Fractal properties are independent of many of the details of the system and are useful parameters for characterizing the geometrical properties of clusters. The kinetics of cluster formation can be studied through the evolution of the cluster size distribution and its moments. The dynamic scaling approach for the cluster size distribution will be presented, and it will be shown how the the kinetics of cluster growth can be described using this general and powerful approach. Theoretical ideas for analytically calculating the cluster size distribution using a Smoluchowski rate equation approach will also be discussed.

26. Identification of Clusters in Phase Transitions

W. Klein and H. Gould
Department of Physics
Boston University
Boston, Massachusetts 02215

Nucleation is one of the most important and common processes in nature. It appears in phenomena as diverse as alloy formation, fracture and protein folding. In order to fully understand and hence control the process, it is essential that we obtain the structural and kinetic properties of the object that initiates nucleation; the so-called critical droplet. Near the coexistence curve, where classical nucleation is the dominant mechanism, identifying critical droplets is simple; we look for isolated spatial regions in the metastable state that have the structure of the stable phase. For example, in a crystallization problem we look for isolated regions in the metastable fluid with the structure of the stable crystal. However, far from the coexistence curve classical nucleation no longer is valid, and the identification of the critical droplet is considerably more complicated. Moreover, it is precisely the quenches far from the coexistence curve that are the most technologically important.

In order to identify the critical droplet far from the coexistence curve we must be able to specify the geometrical characteristics of thermal fluctuations. The work we will discuss deals with how these clusters are identified in both metastable magnetic systems and supercooled fluids undergoing crystallization. Our work, both theoretical and numerical (Monte Carlo and molecular dynamics simulations), indicate that in quenches far from the coexistence curve, the critical droplets are diffuse objects which can, in the magnetic systems, be classified as fractals.

27. Long Time Tails, Anomalous Diffusion and Periodicity for the Autocorrelations of Diffusion in Disordered Media

Hisao Nakanishi and Donald Jacobs
Department of Physics
Purdue University
West Lafayette, Indiana 47907

We propose the structure of leading and correction terms in the mean end-to-end displacement and autocorrelation functions for random diffusion in disordered lattices. This structure incorporates some forms of the long-time tails and the regular oscillations recently found in certain autocorrelation functions of so-called *myopic* random walks on several *fractal* substrates. Some predictions of the proposed structure are confirmed on two- and three-dimensional lattices at the percolation threshold, using a numerical technique which performs the exact summation of all Brownian paths starting from all points of any given finite cluster on a lattice. On bipartite clusters, a scaling law is obtained for the autocorrelations which leads to an approximately superuniversal behavior (in the same way as the so-called Alexander-Orbach conjecture gives approximate superuniversality). An extension of the Langevin theory to anomalous diffusion will also be discussed.

28. Clusters and Percolation in Magnetic Transitions

R.V. Chamberlin, D.N. Haines, and D.W. Kingsbury
Department of Physics
Arizona State University
Tempe, Arizona 85287

We have measured the magnetization of several magnetic systems from 10^{-5} to 10^4 seconds after removing an applied field. The quality and range of the data is sufficient to demonstrate clear deviations from all empirical formulae previously used to fit the magnetic relaxation in similar systems. A simple model which considers the relaxation of a percolation distribution of cluster sizes, with a relaxation rate which depends exponentially upon inverse cluster size, is found to give excellent agreement with the observed behavior.

29. Dynamic Percolation

Raymond Orbach
Department of Physics
University of California
Los Angeles, California 90024

We have been exploring the consequences of carrier hopping motion in an environment where the disorder is dynamic. A specific example found in nature is electrical transport in sodium β"-alumina. Here, the sodium ions diffuse along a two-dimensional hexagonal network of available sites. Upon doping with, for example, Ba^{++} ions, the available sites are randomly reduced in number, the Ba^{++} ions "blocking" the sites available to the Na^+ ions. This leads to percolative behavior for Na^+ ion motion. However, upon warming, the Ba^{++} blockers begin to move themselves. This leads to quite unusual frequency dependences for the electrical conductivity of such a material.

We have calculated the frequency dependent electrical conductivity, $\sigma(\omega)$, of such dynamic structures. In addition, we have been able to add correlation effects by allowing for differing probabilities for the Na^+ ion to hop back to its original site as compared to hopping to new sites.

We have carried out experimental measurements of $\sigma(\omega)$ in sodium β"-alumina doped with various concentrations of Ba^{++} ions. At roughly 70% Ba^{++} doping, the percolation threshold for single ion Na^+ motion is reached, at a Na^+ concentration of only 16%. This means that the coulomb correlations amongst the carrier ions can be reduced to a minimum, allowing for a direct determination of singe particle contributions to the electrical conductivity.

Remarkably, hopping in a dynamic environment can be shown to map onto the problem of the magnetic excitations of an antiferromagnet with a time varying exchange coupling. We believe this to be a description of the Heisenberg antiferromagnet in two dimensions, where holes on the ligand sites are mobile, allowing for time varying super-exchange paths. It is therefore a description of the dynamical excitations of the magnetism of high temperature superconductors. We are currently attempting a (very complex) LaPlace transform of our dynamic percolation equations to obtain the magnetic excitation spectrum of high temperature superconductors in the conducting phase. This is an example of how new developments in one area of science inform the interpretation of another.

30. A Lattice-Free Theory of Clustering

George Stell
Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794-3400

In the context of lattice models, many important aspects of clustering have been successfully described in the language of percolation theory. There are significant features of real clustering phenomena, however, that do not naturally lend themselves to a lattice description. Moreover, the fundamental notions of clustering and percolation have nothing to do with lattices per se. In response to these observations, my colleagues and I have initiated a long-term development of a generalized form of percolation theory that does not hinge on lattice concepts in order to provide a unified framework for describing and treating diverse clustering phenomena. These include nucleation and condensation of gases, gelation, polymerization, the clustering of inclusions in composite media, and chemical association, as well as an interesting class of problems in what has come to be called stochastic geometry. Finally we hope to be able to treat the standard lattice percolation problems in new ways, using new approximation procedures and gaining new insights that are naturally suggested by the novel aspects of our formalisms.